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# A low-energy electron diffraction study of potassium–oxygen coadsorption phases on Ni(111)

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**Abstract.** The coadsorption of potassium and oxygen on a Ni(111) surface has been studied by low-energy electron diffraction (LEED). The initial potassium-induced structures on the bare and the oxygen-monolayer-covered surface exhibit similar LEED ring patterns, which may be attributed to the strong dipole–dipole repulsive interaction in both cases. On the other hand, a small amount of pre-adsorbed oxygen ( $\theta_{\text{O}} < 0.1$ ) prevents the formation of the potassium ring phase, suggesting an attractive K–O interaction. Once all of the pre-adsorbed oxygen is attached to the potassium adatoms, further potassium adsorption produces the same phases as on the oxygen-free surface. For intermediate O precoverages, a gradual structural transformation from a  $p(2 \times 2)$  to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase is observed upon K adsorption. Potassium reduces the critical oxygen coverage for the completion of this phase transformation, suggesting that (disordered) K mixes in the O layer. At higher O precoverages, coadsorption results in a new  $c(4 \times 2)$  ordered phase in a structure which probably involves both K and O.

## 1. Introduction

The study of coadsorption of alkali metals with gases such as oxygen has remained an active field for several decades [1, 2]. This is partly due to the technological applications of alkali adsorption in fields such as catalysis and photocathode fabrications [3]. From a fundamental point of view, alkali metal coadsorption with oxygen is a very challenging subject because of the great variety of new chemical and physical phenomena which are observed. Spectroscopic studies of this system have been conducted on various substrates over the years in order to address the electronic, vibrational and bonding properties. However, the structural aspects of these coadsorption systems have remained largely unexplored until very recently [4–10]. Structural information is clearly a key input for understanding the chemical and electronic properties for these systems. The rich structure of the phase diagrams of coadsorption systems can also provide useful information for studying adsorbate–adsorbate and adsorbate–substrate interactions. The complexity of these coadsorption systems and the lack of detailed structural information on the adsorbed alkalis have hindered progress [11]. Since both K/Ni(111) and O/Ni(111) are very well-characterized systems, we have taken this opportunity to study the potassium and oxygen coadsorption on a Ni(111) surface.

A starting point of this work is our existing knowledge of both potassium and oxygen adsorbates separately adsorbed on the Ni(111) surface. The density–temperature phase

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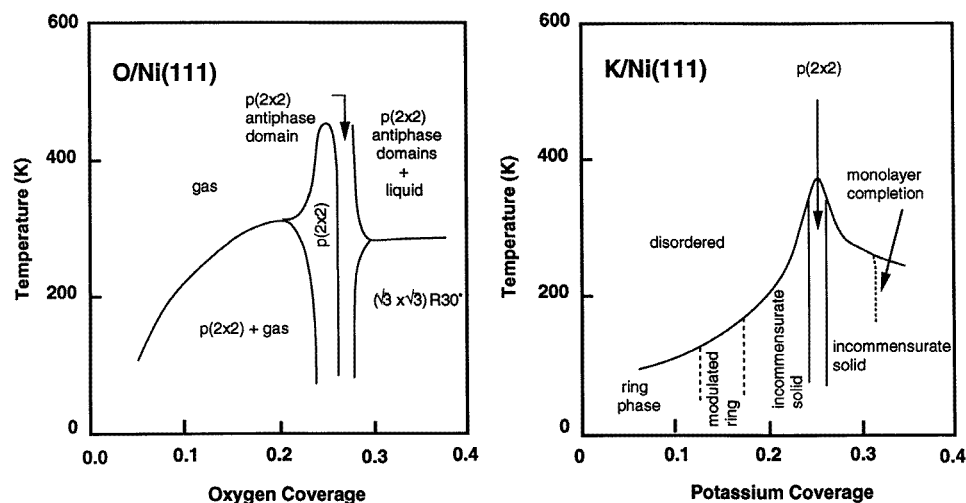


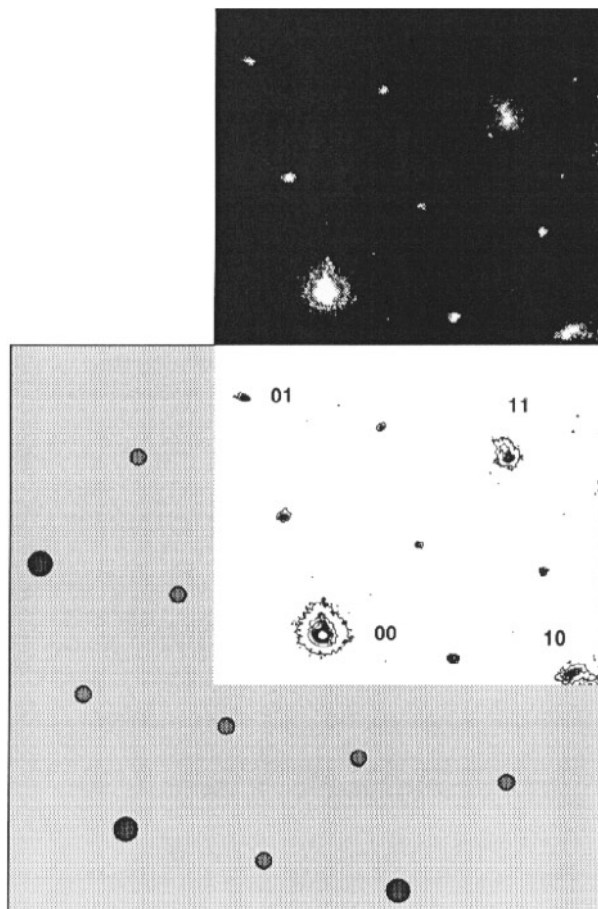
Figure 1. Density phase diagrams for O/Ni(111) and K/Ni(111) [12, 14].

diagrams for both O/Ni(111) [12] and for K/Ni(111) [13, 14] have been studied extensively and are shown in figure 1. The geometric adsorption sites for both systems have also been determined by dynamic LEED analysis: an oxygen atom in the  $p(2 \times 2)$  phase of O/Ni(111) adsorbs at the threefold fcc hollow site [15], and a potassium adatom in the  $p(2 \times 2)$  phase of K/Ni(111) adsorbs at the top site [16], respectively. Upon coadsorption of these two adsorbates, we have observed a variety of new ordered overlayer structures using low-energy electron diffraction (LEED). Based on these results, we have constructed a schematic  $\theta_K - \theta_O$  phase diagram for O + K/Ni(111). In this paper, we will discuss our results in terms of the competition of the adsorbate–adsorbate interaction with the adsorbate–substrate interaction.

## 2. Experimental details

The experiments were carried out in an ultra-high-vacuum system with a base pressure of  $5 \times 10^{-11}$  mbar, which is equipped with a spot-profile-analysis low-energy electron diffraction (SPA-LEED) optics for structural studies and a cylindrical mirror analyser for Auger electron spectroscopy (AES) measurements. The Ni crystal was cut to within  $0.25^\circ$  of the (111) surface which was subsequently mechanically polished and chemically etched. The crystal had been cleaned through many cycles of  $\text{Ar}^+$  bombardments and annealings. Previous studies on O/Ni(111) [17] and K/Ni(111) [14, 16, 18] were carried out using this crystal. Each measurement was done after additional  $\text{Ar}^+$  bombardment and subsequent annealing to 980 K for 15 minutes, and then the sample was allowed to cool down slowly at a rate of about  $1 \text{ K s}^{-1}$  in order to minimize the surface defect density. Oxygen was dosed onto the crystal at a temperature of 240 K through a leak valve with a 6 mm diameter tube which pointed directly at the surface. The oxygen dosage was monitored by a quadrupole mass spectrometer. The oxygen precovered crystal was then allowed to cool down to about 160 K for further potassium adsorption. The K deposition was done through heating a SAES Getters source which had been carefully and sufficiently degassed. During K deposition the background pressure was kept below  $3 \times 10^{-10}$  mbar.

LEED experiments were performed at normal incidence with a beam current of less



**Figure 2.** A SPA-LEED image from an oxygen  $p(2 \times 2)$  phase on Ni(111) surfaces. The bottom panel is the contour plot together with drawings of some diffraction beams out of the SPA-LEED viewing range.

than  $0.1 \mu\text{A}$ , either with a transparent phosphor screen for visual inspection of the pattern or in its channeltron mode for the measurement of the intensity. In the latter mode, the diffraction pattern is recorded by scanning the beam over the channeltron aperture located at a fixed position, using two sets of electrostatic deflection plates [19]. An example of such a LEED pattern for an oxygen  $p(2 \times 2)$  phase on Ni(111) is shown in figure 2. A contour plot is also shown together with a drawing of some diffraction beams out of the SPA-LEED viewing range. In the latter part of the paper, only schematic LEED patterns will be presented.

Throughout the paper, a coverage of one monolayer is defined as having the same number of atoms as a perfect Ni(111) surface layer. The potassium coverage was determined by measuring the dose of potassium required to form a  $p(2 \times 2)$  LEED pattern, which was defined to be a coverage of 0.25 from geometric considerations [14]. Potassium coverages for other structures were then calculated via the deposition time. A saturated monolayer for potassium consists of one close-packed layer of adsorbate atoms and occurs at a coverage of approximately 0.31 for K/Ni(111) [14]. Oxygen coverage is determined in a similar

way, since Auger scans indicated a constant sticking coefficient until the formation of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase occurred at about 1/3 coverage. Again the maximum ordering of the  $p(2 \times 2)$  structure was assumed to take place at 0.25 coverage. Oxygen on the Ni(111) surface forms a stable NiO compound at coverages above 0.5 [20].

Most coadsorption work published so far has been performed using an adsorption sequence of alkali metal followed by oxygen. It has been well documented that the alkali metal promotes oxygen adsorption on single-crystal metal substrates, i.e. the oxygen sticking coefficient increases [1]. This leads to a common problem of oxygen coverage determination for the coadsorption study. Being aware of this problem, we used the opposite adsorption sequence of oxygen followed by potassium. Our AES measurements indicated that the sticking coefficient for potassium was the same on the Ni(111) surface with and without oxygen at least at a substrate temperature of 160 K for the first monolayer. Hence we can derive the potassium coverage directly from the potassium deposition time.

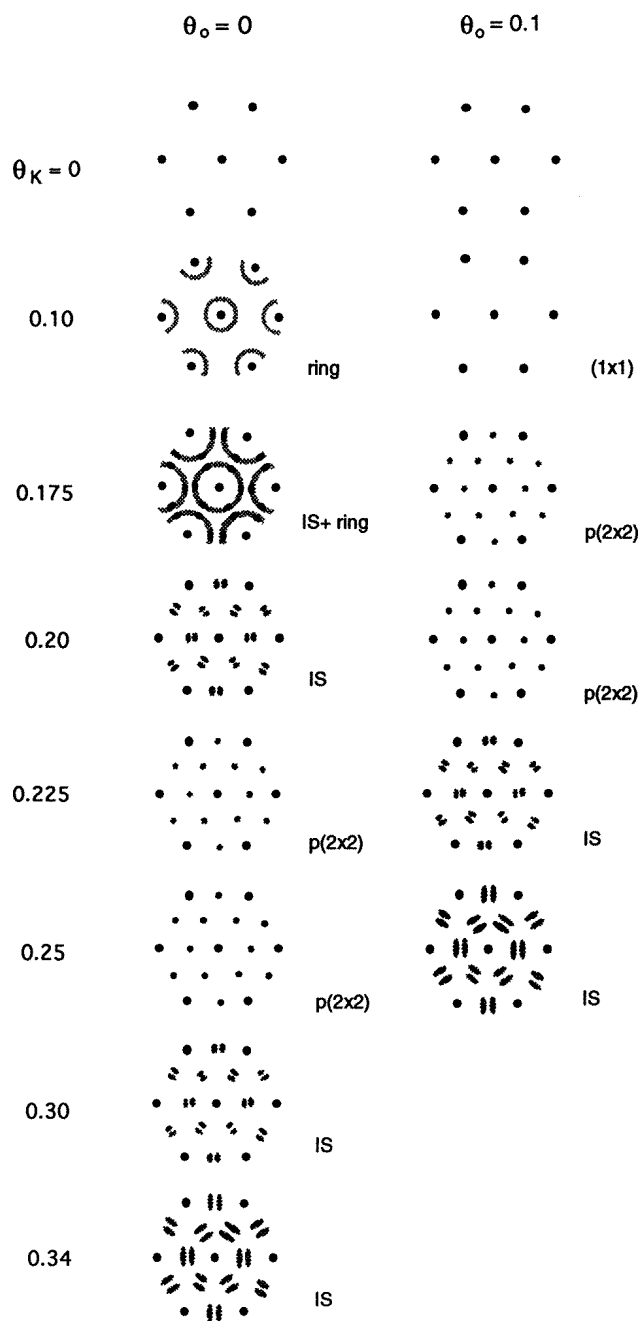
### 3. Results and discussion

#### 3.1. The low-oxygen-coverage regime

The sequence of phases which are observed as a function of K coverage with no pre-adsorbed O are shown in figure 3. These are identical to those observed previously [14], and correspond to a continuously compressing hexagonal-symmetry overlayer. In the coadsorption experiments, the lowest pre-adsorption oxygen coverage was about 0.1. For this coverage of oxygen on Ni(111), no new diffraction features were induced except a slightly increased background intensity, in agreement with previous results [12]. Upon subsequent potassium adsorption, the structure remains as  $(1 \times 1)$  until about  $\theta_K = 0.15$  where half-order diffraction spots gradually develop with increasing K coverage. At a K coverage of 0.225, the half-order spots start to split, with the splitting increasing with further coverage increases. Annealing this phase from 160 to 260 K improves the ordering of this phase but does not appear to alter its structure. Figure 3 shows schematic drawings of some of these LEED patterns.

The most obvious effect of a small amount of pre-adsorbed oxygen on the potassium overlayer is that it prevents the formation of the potassium ring phase and the angularly modulated phase as well as the incommensurate solid phase in K/Ni(111) for  $\theta_K < 0.25$  [14, 21]. The appearance of a ring phase is a general feature for low coverages of alkali metals on metal substrate surfaces [22, 23] and it arises from an alkali metal overlayer with a reasonably well-defined nearest-neighbour distance but lacking long-range rotational order (often denoted as a 'fluid phase'). In the fluid phase, K atoms have a high mobility on the surface. The effect of the pre-adsorbed O must be to disrupt the formation of this phase, possibly by limiting the mobility of the K atoms on the surface or by broadening the distribution of K nearest-neighbour distances. These effects might also be expected to occur if there were an increase in the substrate potential corrugation relative to the strength of the K–K repulsive interaction.

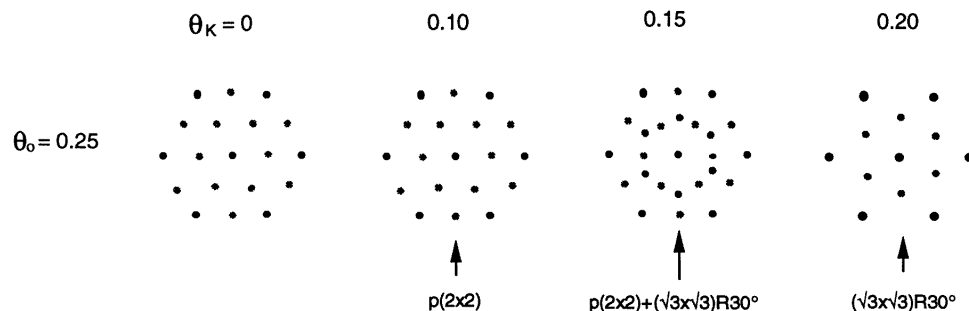
Figure 3 also shows that at higher K coverages the resulting coadsorption phases are similar to those for K/Ni(111), although the K coverage required to form the  $p(2 \times 2)$  phase and the incommensurate solid (IS) phase are smaller than for K-only adsorption. The 0.1 coverage of oxygen corresponds to about 30% saturated monolayers. If we assumed that those sites occupied by oxygen were no longer available for K adsorption, there would be only 70% of the Ni sites remaining free for K adsorption. Thus only 0.18 ( $=0.25 \times 0.7$ ) and 0.21 ( $=0.3 \times 0.7$ ) K coverage is needed to form the  $p(2 \times 2)$  and the IS phases, respectively, on



**Figure 3.** Schematic drawings of LEED patterns obtained for potassium adsorption on clean Ni(111) and on low oxygen precoverages ( $\theta_{\text{O}} = 0.1$ ). IS: incommensurate solid phase.

the oxygen precovered surface. These values are in agreement with our results, suggesting that the pre-adsorbed oxygen results in ‘blocking’ the potassium adsorption, i.e. the oxygen reduces the available Ni surface for direct K adsorption. This result also implies that the

$p(2 \times 2)$  and incommensurate solid phases observed in this case are due to K overlayers, and the randomly distributed oxygen adatoms contribute only to the diffuse background. Similar results were observed for O + K/Ni(100) [10] and O + Cs/Ru(0001) [4] for small doses of oxygen.



**Figure 4.** Schematic drawings of LEED patterns obtained for potassium adsorption on intermediate oxygen precoverages ( $\theta_{\text{O}} = 0.25$ ).

### 3.2. The medium-oxygen-coverage regime

For O coverages in the range  $0.10 < \theta_{\text{O}} \leq 0.25$ , oxygen on the clean Ni(111) surface at 240 K forms a commensurate  $p(2 \times 2)$  phase. Coadsorbing potassium at this O coverage results in a structural transformation from a  $p(2 \times 2)$  to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase via a region of coexistence of these two phases. As expected for a coexistence region, the intensity of the  $\sqrt{3}$  beams increases with increasing coverage at the expense of the half-order beams, until the latter disappear at a coverage  $\theta_{\text{K}} = 0.20$ . Additional K deposition only results in an enhancement of the background intensity, although annealing the surface from 160 to 260 K can restore some of the structural ordering. These results are shown schematically in figure 4 for  $\theta_{\text{O}} = 0.25$ .

A distinct feature of the K-induced structural transformation from a  $p(2 \times 2)$  to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase is its dependence on the coverages of both adsorbates: the smaller the pre-adsorbed oxygen coverage, the larger the potassium coverage required to complete this transformation. Although the exact nature of the overlayer structure involved still awaits more detailed investigations, we may discuss three possibilities.

(1) The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase is due solely to the potassium overlayer. Although such a phase is not stable on Ni(111) at high K coverage [14], it has been observed on other substrates having hexagonal symmetry, e.g. Pt(111) [24, 25], Rh(111) [26], Ru(0001) [27–30] and Ag(111) [31]. However, all of those substrates have a slightly larger in-plane substrate spacing. The overlayer structure dependence on substrate in-plane spacing may have a simple explanation, according to Benesh and Hester [32]. Based on their surface LAPW calculation for the Na/Al system, they suggested that the close spacing of neighbouring alkali metal adatoms in a commensurate structure would necessarily draw more electrons between adatoms to screen nuclei, at the cost of increasing their kinetic energy due to Pauli exclusion. At the same time the interlayer charge transfer is reduced, weakening the adsorbate–substrate (A–S) interaction. In K/Ni(111), the kinetic energy of the interlayer electrons may be lowered through the incommensurate structure because of weaker A–S interaction. If the potassium is adsorbed on the top of an oxygen adlayer in the

K/O/Ni(111) system, the increased corrugation potential seen by potassium may stabilize the commensurate structure either by enhanced A–S interaction or by additional screening of alkali nuclei by oxygen adatoms. On the other hand, if one assumes that K would prefer to adsorb first directly on the Ni surface rather than on the oxygen-covered surface (which is consistent with the case of low oxygen precoverage), it would explain why extra K is required to complete this transformation for the case where there is less oxygen in the  $p(2 \times 2)$  island phase. However, the fact that the actual K coverage is 0.20 in this phase rather than 0.33 makes this picture less convincing. An alternative explanation is the formation of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase by K directly on the Ni surface. This scenario necessarily involves the dissolution of the ordered oxygen islands and the random incorporation of oxygen into the potassium structure. However, this is not consistent with the result that for smaller amounts of O pre-adsorption, larger amounts of K are necessary to form this structure.

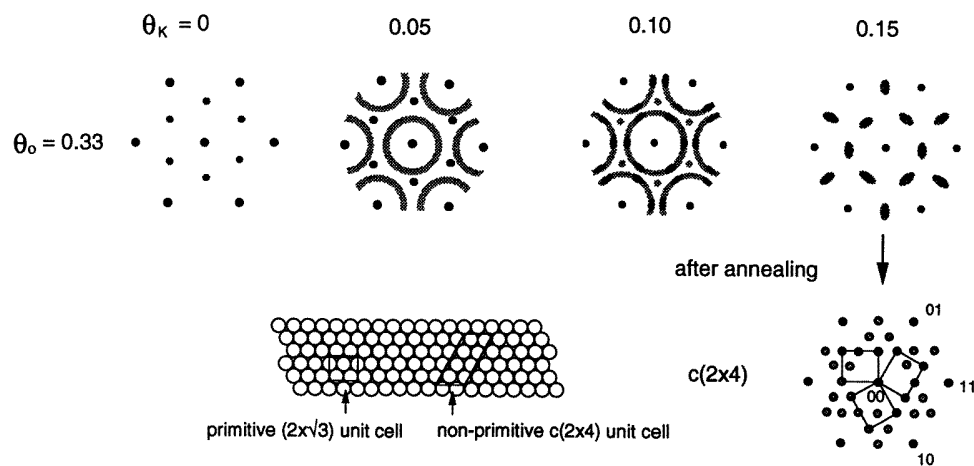
(2) Another possibility is that the commensurate structural transformation from  $p(2 \times 2)$  to  $(\sqrt{3} \times \sqrt{3})R30^\circ$  is a result of oxygen ordering on its own, with the potassium randomly distributed and contributing only to the LEED diffuse background. A similar transition does occur for O on a clean surface of Ni(111) between coverages of 0.25 to 0.33 [12, 17], except that in that case there is an intermediate incommensurate phase between the two commensurate phases. Such an explanation would suggest that the presence of K seems to reduce the critical oxygen coverage required for the completion of this phase transformation. One argument in support of this explanation is that the K coverage responsible for starting this transformation is so small that it would only produce the ring phase if it were on the clean Ni(111) surface. This model then can be thought of as the opposite to the case of low O coverage, where the O atoms are seen to block K adsorption. In this model, the K atoms would effectively ‘block’ O adsorption sites with the variation that oxygen is already on the surface. As a result of that, K adatoms effectively introduce a lateral force which compresses the oxygen adatoms within the  $p(2 \times 2)$  islands leading to the structural transformation. The lack of an incommensurate phase intermediate between the  $p(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phases could arise from the K atoms interfering with the long-range O interactions which contribute to that phase [12]. This model is also consistent with the observation that for smaller initial amounts of O, larger amounts of K are required to form the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure.

(3) The final possibility is that it is a cooperative structure due to potassium and oxygen. In other words, the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure is an ordered structure in which both the O atoms and the K atoms participate in the ordering. Such cooperative structures have been observed in other systems and some of their geometries have been determined [4, 5, 7]. However, a cooperative structure would suggest that there should be a constant or preferred K:O stoichiometry, which is not observed.

### 3.3. The high-oxygen-coverage regime

Pure oxygen adsorption on Ni(111) results in a saturated monolayer with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. Upon coadsorption of potassium on the  $O-(\sqrt{3} \times \sqrt{3})R30^\circ$  phase, formation of a ring phase in coexistence with the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase was observed initially, as shown in figure 5. The diameter of the rings increased as potassium coverage increased just like for K on a clean Ni(111) surface, and at the same time the  $\sqrt{3}$  beams became weaker. At a K coverage of 0.15, the  $\sqrt{3}$  beams were no longer visible and diffuse spots were present at the half-order positions. The background intensity was also higher. Annealing this overlayer to 270 K resulted in a new ordered structure of  $c(4 \times 2)$  symmetry. The schematic LEED pattern of this phase is shown in figure 5 together with the corresponding





**Figure 5.** Schematic drawings of LEED patterns obtained for potassium adsorption on high oxygen precoverages ( $\theta_{\text{O}} = 0.33$ ). The primitive ( $2 \times \sqrt{3}$ ) unit cell and non-primitive  $c(2 \times 4)$  unit cell in real space are also shown.

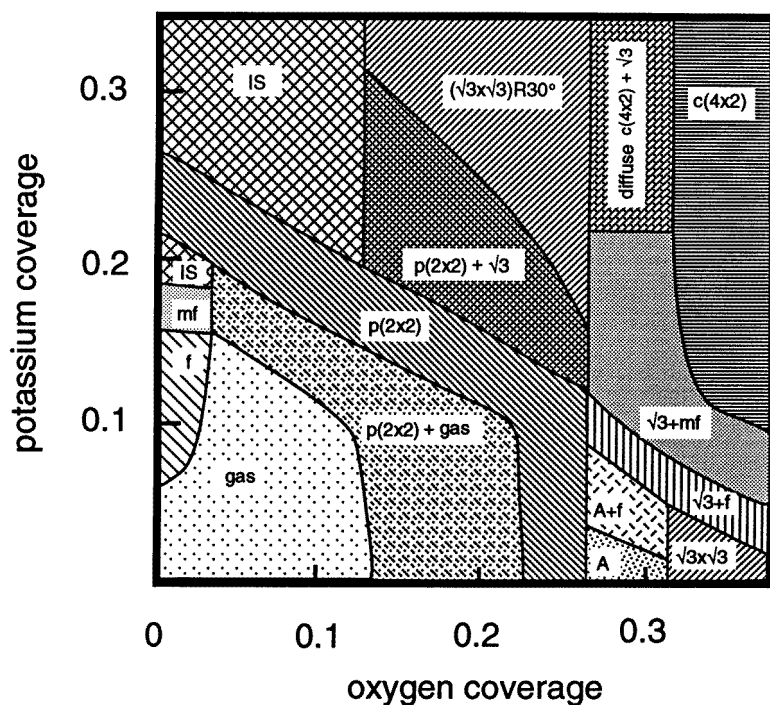
unit cells of one domain in real space. Further deposition of potassium on the  $c(4 \times 2)$  phase did not produce new structures. This  $c(4 \times 2)$  phase could also be prepared by reversing the dose sequence, i.e. potassium first, followed by oxygen adsorption. Starting with the pure potassium  $p(2 \times 2)$  phase, oxygen adsorption at 260 K first led to the half-order spots becoming weaker and broader, and then the  $c(4 \times 2)$  phase appeared for oxygen dosage above  $0.007 \text{ L}\dagger$ . For a substrate temperature of 155 K, formation of the  $c(4 \times 2)$  phase required annealing to above 210 K. When the oxygen precoverage was just below 0.3 monolayer, the high potassium dosage resulted in the appearance of the  $c(4 \times 2)$  phase coexisting with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase after annealing to 270 K. According to the phase diagram in figure 1, the antiphase domain structure occurs in this oxygen coverage range. In fact, we only observed  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase coexistence with very broad half-order beams. This may be due to the limited angular range of detection of the SPA-LEED screen, making very diffuse features difficult to observe. In this range of coadsorption, we will discuss the two main features, namely the evolution of the ring phase and the  $c(4 \times 2)$  phase.

**3.3.1. The ring phase.** As we pointed out previously, the ring phase is a common feature in alkali metal adsorption on metallic substrates, and results from the strong mutual repulsion between K adatoms. The observation of the ring phase has not been reported before for coadsorption studies. The existence of the ring phase suggests that the K remains on top of the O layer instead of mixing with it, and the surface potential corrugation for K on a full monolayer of oxygen on Ni(111) is relatively small such that the K–K repulsion is still dominant over the K–O/Ni interaction. Other coadsorption studies on metal substrates with hexagonal symmetry have been exclusively conducted at constant alkali coverage while varying the oxygen dose. We have also examined coadsorption in the same sequence. First we prepared the pure potassium ring phase at 180 K and then exposed it to oxygen. The initial oxygen coadsorption destroyed the potassium ring phase and resulted in a  $(1 \times 1)$

$\dagger$  ( $\text{L} \equiv \text{Langmuir}$ .) This exposure is calculated from the partial pressure of oxygen measured by a mass spectrometer in the system. As a reference,  $0.05 \text{ L}$  of oxygen in our case produces one monolayer of O on Ni(111) surfaces at 160 K. Pre-adsorbed potassium would generally promote oxygen adsorption on surfaces.

structure. Upon further oxygen exposure, a  $p(2 \times 2)$  phase gradually emerged. At 0.007 L, the  $p(2 \times 2)$  phase was very diffuse. Annealing the overlayer increased some ordering but did not restore the ring phase. Although it has been proposed that oxygen generally bonds preferentially with the substrate for adsorption in either sequence [2, 33], our results seem to suggest that when K was adsorbed first, it did not get promoted to the top layer when subsequent oxygen was adsorbed—otherwise the ring phase would be expected.

**3.3.2. The  $c(4 \times 2)$  phase.** So far, we have no detailed knowledge of the structure of the  $c(4 \times 2)$  phase, but the fact that it can form over a range of stoichiometries and that annealing is required if adsorption takes place at low temperature suggests that it is a structure in which there is K–O order. This could be in the form of a molecular complex or simply mixed overlayer ordering [4, 5]. This is consistent with the observation that the formation is independent of the dose sequence. We note that for O + K/Ni(100) similar commensurate phases have been observed [9, 10, 34].



**Figure 6.** The proposed phase diagram for K + O/Ni(111). f: fluid phase; mf: modulated fluid phase; IS: incommensurate solid; A: antiphase domain phase.

#### 4. Summary and conclusion

We have summarized the above results in the schematic ‘phase diagram’ shown in figure 6. One of the characteristic features of the phase diagram is the occurrence of the ring structure at the bare surface and on the monolayer-oxygen-pre-adsorbed Ni(111) surface. In both cases, we interpret this as being a fluid phase of potassium where the dominant force is the

lateral repulsion-between potassium adatoms. However, we found that this repulsion-driven phase terminated at a smaller potassium coverage on the oxygen-covered surface than on the bare surface. This suggests that (1) potassium adsorbs on top of an oxygen monolayer, and (2) the K surface potential corrugation is stronger on the O/Ni system than on the Ni surface.

We also found that a small amount of pre-adsorbed oxygen ( $\theta < 0.1$ ) could easily prevent the formation of the potassium ring phase. In this case, we may assume that both potassium and oxygen adsorbates were bonded to the substrate. It appears that once all of the pre-adsorbed oxygen becomes somehow bound to the K, further K adsorption produces the same phases as on the clean surface.

At higher oxygen coverages, a  $c(4 \times 2)$  phase was observed. It is possible that a  $\text{KO}_x$  compound is formed at these high potassium and oxygen coverages, and that its formation is kinetically hindered at low temperatures since annealing is required.

Much more work is necessary to ascertain the details of the coadsorption structures. However, the results that we have presented here suggest that K and O at low coverages interact strongly with both the substrate and each other, leading to the blocking behaviour described above. For high K and O coverages it seems likely that potassium oxides are formed. A structural study of the  $c(4 \times 2)$  phase would be very interesting.

### Acknowledgments

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